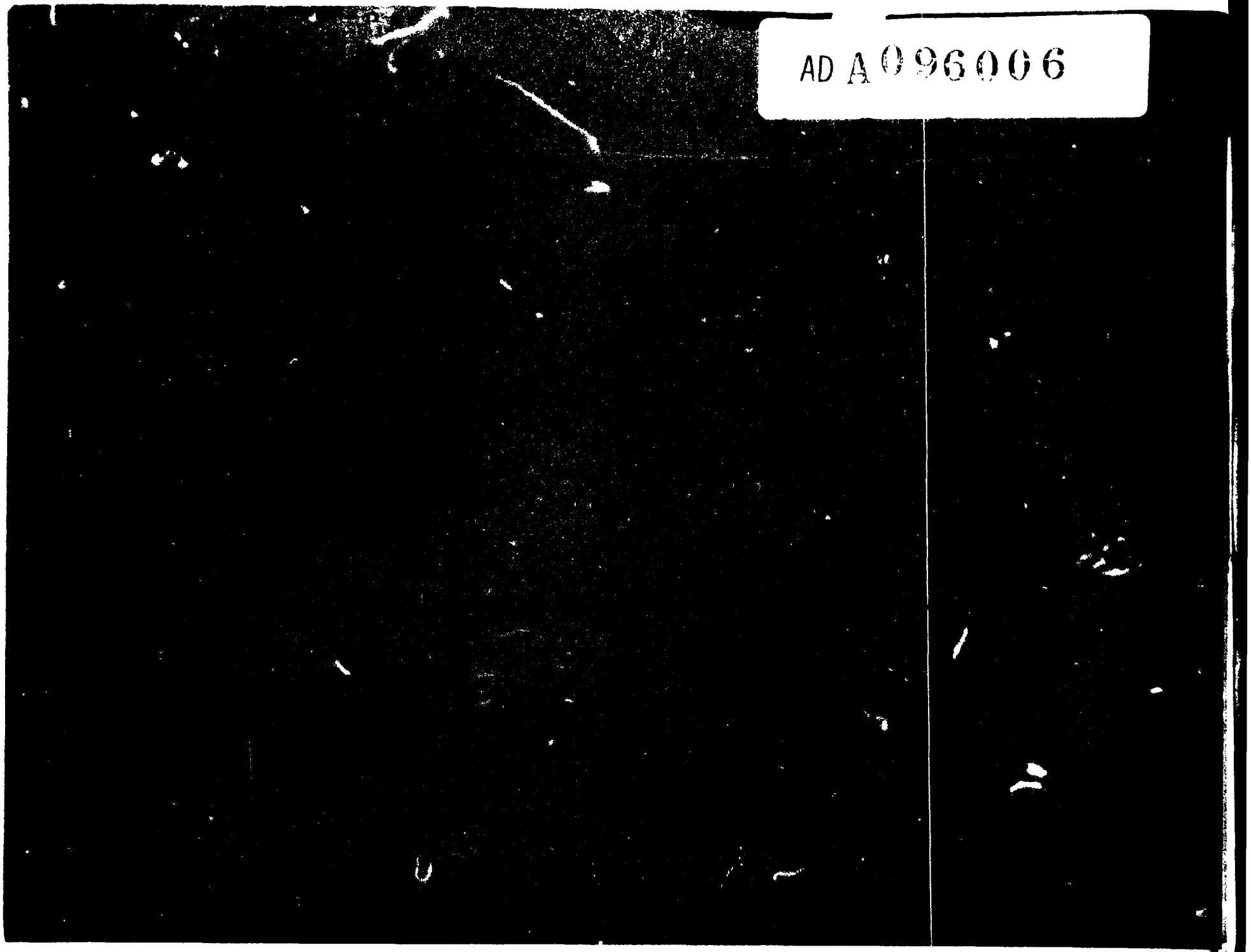
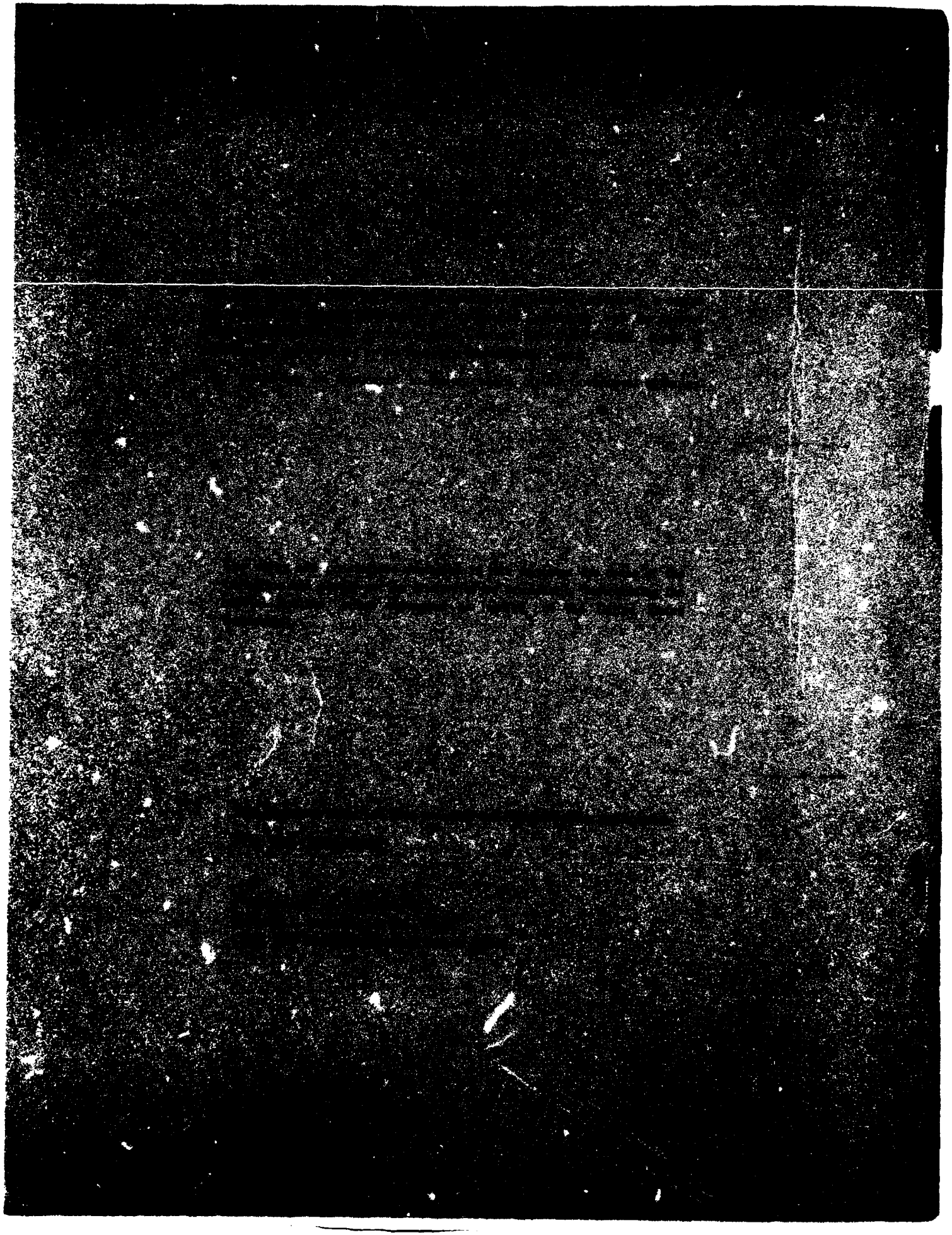
AD-A096 006 MASSACHUSETTS INST OF TECH LEXINGTON LINCOLN LAB F/G 20/2
INP MATERIALS,(U)
SEP 80 G W ISELER F19628-80-C-0002

UNCLASSIFIED ESD-TR-80-231 NL

1 OF 1
AD A096 006

END
DATE FILMED
4-81
DTIC


AD A096006



MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LINCOLN LABORATORY

InP MATERIALS

ANNUAL TECHNICAL SUMMARY REPORT
TO THE
ROME AIR DEVELOPMENT CENTER

1 OCTOBER 1979 – 30 SEPTEMBER 1980

ISSUED 21 JANUARY 1981

Accession For
FTIS GRA&I
DTIC TAB
Unannounced
Justification
By
Distribution/
Availability Codes
Dist
A

Approved for public release; distribution unlimited.

LEXINGTON MASSACHUSETTS

ABSTRACT

This report covers the work on InP materials carried out with support of the Department of the Air Force during the period 1 October 1979 through 30 September 1980. A part of this support was provided by the Rome Air Development Center.

The current objectives of the program are to improve the yield of high-purity polycrystalline InP as source material for crystal growth and to optimize the liquid-encapsulated Czochralski (LEC) method in order to grow high quality crystals with uniform doping concentration and low dislocation density.

We have synthesized polycrystalline InP with mobility at 77 K as high as 8.2×10^4 cm^2 $V^{-1}sec^{-1}$. Electrical measurements have been made on 18 of the 30 ingots synthesized during this report period. More than half of the measured ingots have exhibited mobilities at 77 K greater than 5×10^4 cm^2 $V^{-1}sec^{-1}$. Using such high-purity charge material we have grown Fe-doped LEC crystals with mobility at 300 K as high as 4.6×10^3 cm^2 $V^{-1}sec^{-1}$, and nominally undoped crystals with mobility at 77 K as high as 4.1×10^4 cm^2 $V^{-1}sec^{-1}$.

From our study of the LEC growth of over 100 InP boules we have found that a high yield of twin-free crystals can be achieved if the axial temperature gradient at the melt interface exceeds a certain minimum value. In order to reduce the average dislocation density to values below the 10^4 cm^{-2} range, it will be necessary to decrease the radial temperature gradient. During the coming year we will attempt to accomplish this decrease while maintaining a low twinning probability.

An x-ray topography facility and a CO_2 laser scanning system have been set up to monitor the defect and impurity distributions in LEC crystals.

INTRODUCTION

The goals of the InP materials program at Lincoln Laboratory are the development of reliable techniques for preparing high-quality InP single crystals of controlled electrical properties and the utilization of these techniques to produce crystals needed for research on optoelectronic devices such as GaInAsP/InP diode lasers and detectors.

Our program consists of two components: synthesis of InP from the elements and crystal growth by the liquid-encapsulated Czochralski (LEC) method. Synthesis, which is accomplished by directional solidification of In-rich solutions under controlled P pressure, has been undertaken in order to assure an adequate supply of polycrystalline charge material with the purity desired for LEC growth, since such material is not consistently available from commercial sources. The LEC growth of InP single crystals is made difficult because growing boules have a strong tendency to twin, due to the compound's very low stacking fault energy.[1] Since twinning is generally followed by polycrystalline growth, the yield of useful crystals will be extremely small unless twinning can be prevented. In investigating LEC growth we have therefore concentrated on establishing growth conditions that minimize the probability of twinning but do not result in excessive dislocation densities. We have succeeded well enough to obtain a large number of crystals suitable for device studies, and we are now turning our attention to refining the growth conditions in order to achieve still lower dislocation densities.

SYNTHESIS

Synthesis of InP from the elements is carried out in sealed fused-silica ampoules in a resistance-heated clamshell furnace. Figure 1 shows a diagram of a synthesis ampoule, drawn approximately to scale, together with a typical temperature profile of the synthesis furnace. Initially the ampoule is closed at one end and open at the other. After being vacuum baked at about 1000°C, it is loaded with a charge of red P in chunk form at the closed end and a charge of several 100-g In ingots at the open end, with the In placed in a fused-silica boat 21 cm long that is fabricated from 39-mm-ID tubing. The P is used as received from the supplier, while the In is etched with a series of ultrahigh-purity acids and then rinsed with deionized water. The P and In charges, which typically weigh 135 and 500 g, respectively, are separated by means of an evacuated, sealed fused-silica plug that closely fits the ampoule with a clearance of less than 2 mm. (Five runs were made with 160 g P and 600 g In, and one used 180 g P and 700 g In.) The plug, which is carbonized on the inside, is used to reduce the convective and radiative transfer of heat from the hot zone to the P reservoir when the ampoule is heated to the synthesis temperature, in order to prevent explosions that could result from overheating the P charge. The loaded ampoule is sealed to a vacuum system by means of a flared fused-silica cap, evacuated with a vac-ion pump to a pressure of less than 10^{-6} Torr while being heated with resistance tape, sealed off, and transferred to the synthesis furnace, which is then heated to give a temperature profile like that plotted in Fig. 1. After the desired profile is achieved, typically in about 6 hours, the ampoule is pulled through the furnace at a rate of about 2.5 cm/day. The temperature of the P reservoir is maintained constant at a value between 420 and 445°C, and the maximum In boat temperature is in the range between 1025 and 1055°C. When synthesis is

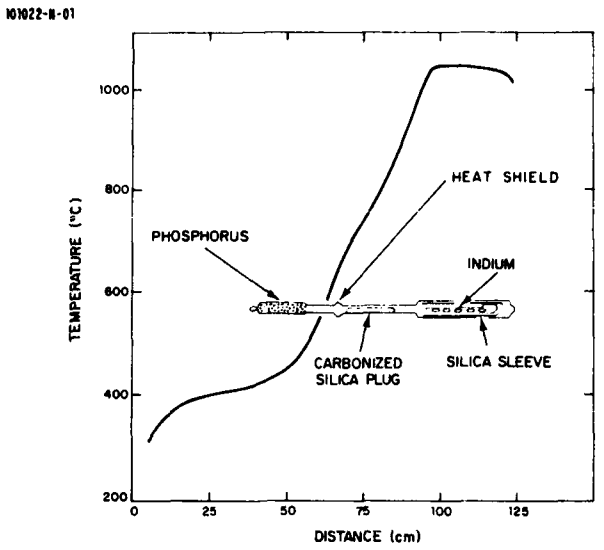


Fig. 1. Ampoule and temperature profile for synthesis of InP.

complete, which requires about 8 days, the furnace power is turned off and the ampoule is furnace cooled.

The synthesis procedure yields ingots that are highly polycrystalline but generally contain one or more grains large enough to permit single-crystal rectangular bars 10 x 3 x 1 mm^3 to be cut out for Hall coefficient and resistivity measurements. The ingots contain In inclusions, but the concentration of elemental In is usually quite low except at the last-to-freeze end.

From October 1979 through September 1980 we have synthesized 30 InP ingots, most of which were prepared from 6 9's In and P (Form I) purchased from M.C.P. Electronics Ltd. Electrical measurements have been made at 300 and 77 K on samples from 18 ingots. All the samples are n-type. Figure 2 shows the distribution of carrier mobilities at 77 K for the 17 measured ingots that were prepared from both M.C.P. In and P. The mobilities range

104621-N

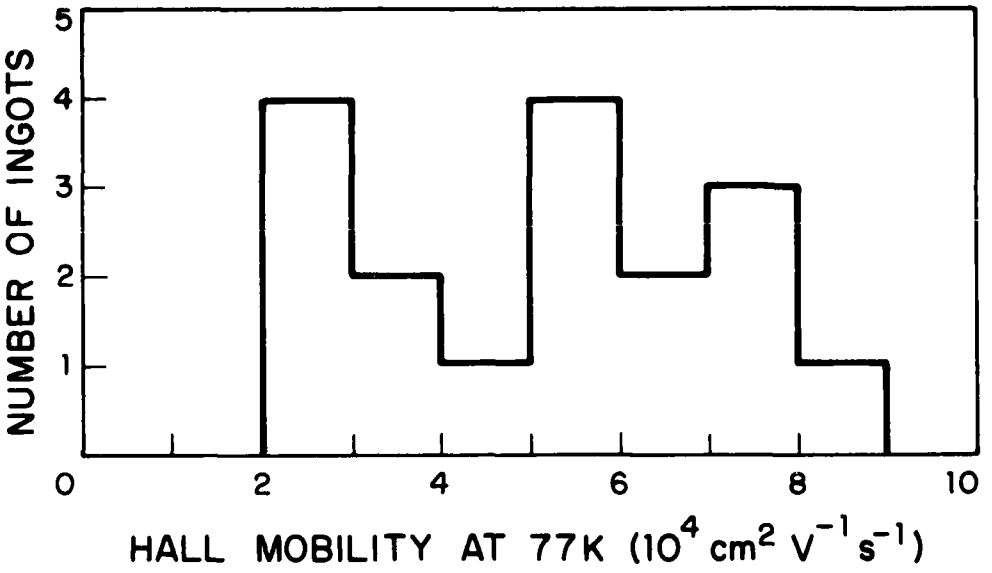


Fig. 2. Distribution of Hall mobilities at 77 K for InP ingots.

from 2.2 x 10^4 to 8.2 x 10^4 $cm^2V^{-1}sec^{-1}$, compared with the highest reported value of 9.1 x 10^4 $cm^2V^{-1}sec^{-1}$.[2] For these ingots the carrier concentrations at 77 K range from 5 x 10^{14} to 8 x 10^{15} cm^{-3}, with the concentration generally increasing as the mobility decreases. (Prior to this reporting period mobilities as low as 8.2 x 10^3 $cm^2V^{-1}sec^{-1}$ and carrier concentrations as high as 2.8 x 10^{16} cm^{-3} were measured at 77 K for ingots in which at least one of the starting elements was obtained from a source other than M.C.P.) No correlation has been found between the measured mobility and the P reservoir temperature, the In boat temperature, or any other aspect of synthesis procedure. For samples with mobilities less than about 2.5 x 10^4 $cm^2V^{-1}sec^{-1}$ at 77 K the Si concentration determined by mass spectrographic analysis generally increases with increasing carrier concentration. For samples with higher mobilities, the Si concentration is so low that the mass spectrographic data are not sufficiently reliable to determine whether or not there is a

correlation between the Si and carrier concentrations. Table I lists the impurities found by mass spectrographic analysis of samples from two different ingots, with carrier concentrations at 77 K of 1.2×10^{15} and 1.9×10^{16} cm^{-3}, respectively. The Si concentrations detected were 0.8×10^{15} and $2.2. \times 10^{16}$ cm^{-3}, respectively.

LEC CRYSTAL GROWTH

The second component of our InP materials program is the LEC growth of single crystals. A systematic investigation has been carried out to determine the effect of changes in the growth parameters on the probability of twinning. The results of this investigation, which we will describe in detail later, support the conclusion that a certain minimum temperature gradient at the crystal-melt interface is necessary to prevent twinning, and they indicate that this minimum is increased by the presence of high concentrations of certain dopants (in particular Zn, and perhaps S). On the basis of these results we have developed a standard growth procedure that for other dopants produces a high yield of boules that are twin-free over most of their length, although twinning generally occurs close to the lower end, where the temperature gradient is reduced because the growth interface is near the bottom of the crucible.

The LEC growth is carried out in a high-pressure crystal puller (A.D. Little Model HPCZ) with water-cooled walls. A diagram of the assembly used for our standard growth procedure is shown in Fig. 3. The seed is a (111)-oriented crystal, 5×5 mm^2 in cross section, that is mounted with the P face down on a BN holder attached to a water-cooled pulling rod. A pyrolytic BN crucible 6.3 cm in diameter and 4 cm high is loaded with a charge of polycrystalline InP weighing 300 g, the desired weight of dopant (if any),

TABLE I

MASS SPECTROGRAPHIC ANALYSIS OF
POLYCRYSTALLINE InP INGOTS

Ingot 79 E	Ingot 79 V
$n_{77} = 1.2 \times 10^{15}$	$n_{77} = 1.9 \times 10^{16}$
$\mu_{77} = 8.2 \times 10^{4}$	$\mu_{77} = 1.0 \times 10^{4}$

Element	Concentration (ppma)	
K	0.4	0.1
Cl	0.05	0.03
S	0.1	< 0.7
Si	0.04	1.1
Al	0.1	ND
F	0.04	ND
O	0.4	0.7
N	0.02	0.03
C	0.8	0.8

n expressed in cm^{-3}
μ expressed in $cm^2V^{-1}sec^{-1}$
1 ppma $\approx 2 \times 10^{16}$ cm^{-3}
ND = not detected

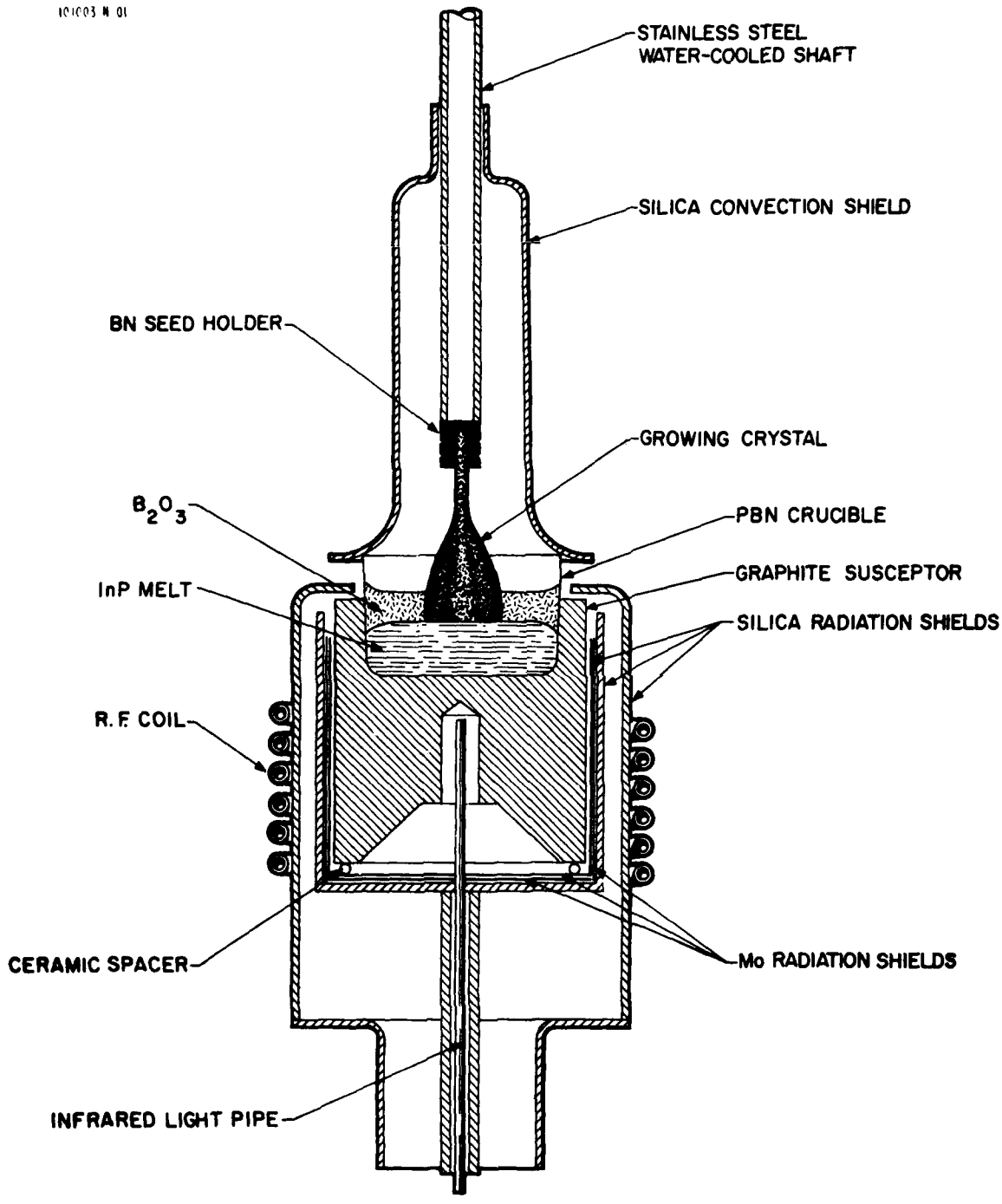


Fig. 3. Assembly for LEC growth of InP cyrstals.

and a charge of B_2O_3 encapsulant weighing 50 g (which gives an encapsulant layer thickness of ~ 10 mm). The B_2O_3 is pre-baked in vacuum at about 1200°C for about 8 hours to reduce its water content. The crucible is placed in a high-purity, high-density graphite susceptor, which is heated by means of an RF coil operated at 200-400 kHz. The RF power is monitored with a pickup coil and controlled by means of a three-mode solid state controller, and the relative temperature of the susceptor is monitored by using a photodiode detector to measure the infrared emission from the susceptor that is transmitted through a fused-silica light pipe. The Mo and fused-silica radiation shields shown in Fig. 3 are used to shape the temperature profile and to keep the RF coil and the walls of the pressure chamber from overheating, while a fused-silica convection shield resting on the crucible is used to reduce the convection currents in the high-pressure gas surrounding the growing crystal. The gas is a 10:1 mixture of high-purity Ar and He with a total pressure of 40 atm. The seed and crucible are rotated in the same sense at rates of 2 and 16 rpm, respectively, and the pulling rate ranges from 15 to 25 mm/h.

Our standard LEC procedure has been used for 70 growth runs. Except for 4 runs made without intentional doping, the starting charge was doped in each case with either Cd, Zn, Sn, S (in the form of GaS), or Fe. The results obtained are summarized by Table II, which lists the number of runs made with each dopant and the percentage of these runs that yielded "untwinned" boules (including boules in which twinning occurred only near the lower end). For Zn and S, the runs in which the boules were doped with concentrations of less than 1×10^{18} cm^{-3} are listed separately from those in which the doping was heavier.

TABLE II

YIELD OF "UNTWINNED" BOULES
OBTAINED BY STANDARD LEC GROWTH PROCEDURE

Dopant	Number of runs	Percentange of "untwinned" boules
None	5	100
Cd	6	83
Sn	8	75
Fe	15	87
$[Zn] < 1 \times 10^{18}$ cm^{-3}	3	100
$[S] < 1 \times 10^{18}$ cm^{-3}	5	80
All of the above	42	86
$[Zn] > 1 \times 10^{18}$ cm^{-3}	26	19
$[S] > 1 \times 10^{18}$ cm^{-3}	2	0

As shown in Table II, a total of 42 growth runs using the standard procedure have been made without intentional doping, with dopants other than Zn or S, and with Zn or S at concentrations below 1 x 10^{18} cm^{-3}. These runs produced 36 untwinned boules, for an excellent overall yield of 86 percent. In striking contrast, for the 26 runs with Zn doping of 1 x 10^{18} cm^{-3} or higher the yield of untwinned boules was only 19 percent. Since the probability of twinning increases as the stacking fault energy decreases, the results suggest that Zn doping of InP decreases the stacking fault energy, as has been reported for Sn doping of GaAs.[3]

There may also be a relationship between the increase in twinning due to heavy Zn doping and the observation by Seki, Watanabe and Matsui[4] that doping with Zn at concentrations in the low 10^{18} cm^{-3} range permits dislocation-free InP crystals to be grown by the LEC method even at high interface temperature gradients. If there is such a relationship, heavy S doping might be expected to increase the probability of twinning, since Seki, et al. also observed such doping to permit the growth of dislocation-free crystals. Thus it may be significant that twinned boules were obtained in both of the runs made with our standard procedure in which the S doping exceeded 1 x 10^{18} cm^{-3}.

As mentioned earlier, in developing our standard procedure for LEC growth we made a systematic investigation of the effect of changes in the growth parameters on the probability of twinning. The results of that investigation are summarized by Table III, which lists each of the parameters studied and the direction of the change in the parameter that was found to decrease the incidence of twinning. In every case a change of the parameter in the direction listed is expected to cause an increase in the temperature gradient at the crystal-melt interface. For example, increasing the susceptor height allows the RF coil to be placed lower relative to the crucible and thus

Table III

LEC GROWTH PARAMETERS THAT AFFECT TWINNING

Growth parameter	Change in parameter that reduces twinning
Crucible height	Decrease
B_2O_3 thickness	Decrease
Heat sinking of seed	Increase
RF coil position relative to crucible	Lower
Susceptor height	Increase
Total gas pressure	Increase
Ratio of He pressure to Ar pressure	Increase
Pull rate	Increase

Table IV

ELECTRICAL PROPERTIES OF NOMINALLY UNDOPED InP CRYSTALS

Crystal Number	Starting Charge		LEC Crystal	
	$n_{77}(cm^{-3})$	$\mu_{77}(cm^2V^{-1}sec^{-1})$	$n_{77}(cm^{-3})$	$\mu_{77}(cm^2V^{-1}sec^{-1})$
268	1.2×10^{15}	8.2×10^4	2.8×10^{15}	4.1×10^4
280	1.0×10^{15}	3.9×10^4	3.0×10^{15}	3.5×10^4
294	8.1×10^{14}	7.2×10^4	4.0×10^{15}	3.4×10^4

increases the vertical temperature gradient. Decreasing the crucible height increases the gradient by reducing the after-heater effect of the crucible walls that extend above the melt. In a detailed study of the LEC growth of GaP crystals, Nygren[5] also found that the probability of twinning was reduced by decreasing the crucible height, and he too attributed this effect to the resulting increase in the temperature gradient. We conclude that one essential requirement for twin-free growth of InP crystals by the LEC method with our crystal puller and its associated RF generator and power controller is that the temperature gradient must exceed some minimum value. This conclusion is not inconsistent with the emphasis placed by Bonner[6] on the rate of diameter increase and interface shape as factors influencing the probability of twinning in InP growth.

The results described earlier on the growth of Zn-doped crystals by our standard LEC procedure indicate that Zn doping above 1×10^{18} cm^{-3} significantly increases the minimum temperature gradient required for twin-free growth. We have therefore carried out several runs in which the growth parameters were changed in the direction expected to increase the gradient. In the six most recent runs, with Zn doping between 1 and 4×10^{18} cm^{-3}, the gradient was markedly increased by decreasing the thickness of B_2O_3 (30 grams were used instead of 50) and also by removing the fused-silica convection shield. Untwinned crystals were obtained in five of the six cases, and the most recent was very nearly dislocation free.

In order to provide an adequate supply of InP for device studies by means of LEC growth, it is necessary not only to achieve a high yield of untwinned crystals but also to insure that these crystals are appropriately doped to give the desired electrical properties. Satisfactory control of the electrical properties also requires that the crystals have an acceptably low

concentration of residual impurities. We have monitored this concentration by periodically growing crystals without intentional doping and characterizing them by means of Hall coefficient and resistivity measurements. Table IV lists the carrier concentration and mobility for samples from three of the undoped crystals, together with the values for the corresponding polycrystalline charges. All the samples are n-type . For the three crystals at 77 K the carrier concentrations range from 2.8 to 4.0 x 10^{15} cm^{-3}, and the mobilities from 4.1 to 3.4 x 10^{4} $cm^{2}v^{-1}sec^{-1}$. In each case the carrier concentration is significantly higher and the mobility significantly lower for the crystal than for the starting charge. Two possible sources for the additional impurities are the B_2O_3 encapsulant and the grain boundaries of the charge material. The impurity concentrations in the undoped crystals are too low for reliable mass spectrographic analysis. However, we do have evidence from proton-induced x-ray analysis that one batch of B_2O_3 contained about 100 ppma of Zn. Mass spectrographic analysis showed that Fe-doped crystals grown with this material as encapsulant were contaminated with Zn at levels in the 10^{15} cm^{-3} range, sufficient to make the crystals p-type instead of semi-insulating. We have recently grown a number of Fe-doped crystals in runs using uncontaminated B_2O_3 (Johnson-Matthey Puratomic 99.9995%). The residual impurity concentrations in these crystals must be quite low, since the crystals are semi-insulating, although the charge doping was only 0.01 w/o Fe. The low residual impurity concentrations are also evidenced by the fact that the mobilities at 300 K are all between 3.5 and 4.6 x 10^{3} $cm^{2}v^{-1}sec^{-1}$, among the highest values so far reported for semi-insulating Fe-doped InP.[7,8]

So far in our investigation of the LEC growth of InP, we have concentrated on achieving a high yield of twin-free crystals with controlled electrical properties. We have paid less attention to the problem of crystal

perfection and consequently have not made measurements of dislocation density for all of the LEC boules. Recently, however, by means of chemical etching we have shown that the first-to-freeze portions of a number of crystals have dislocation densities between 10^3 and 10^4 cm^{-3}, a range that is useful for device studies. We are now attempting to obtain still lower dislocation densities by further adjustment of the LEC growth parameters. In preliminary experiments we have found that the dislocation density is greatly increased by a strong increase in the interface temperature gradient, in contrast with results reported for Si.[9] For example, cracked crystals with dislocation densities of nearly 10^6 cm^{-2} were obtained when the heat sinking of the seed was increased by replacing the BN seed holder with a Cu holder. Thus in order to achieve very low dislocation densities (other than by heavy Zn or S doping) it will probably be necessary to keep the temperature gradient close to the minimum value required to prevent twinning. The etch pits in nearly every recent LEC boule occur in a pattern which indicates that the dislocations are created by stresses caused by an excessive radial temperature gradient. Such behavior was also recently reported by Cockayne, MacEwan, and Brown.[10] A lower radial gradient can almost surely be obtained by using a thicker B_2O_3 encapsulating layer and an afterheater integrated with the silica convection shield, but additional changes will then be needed in order to maintain a low twinning probability. These changes will include improvements in the pulling mechanism to reduce vibrations and replacement of the power control unit on the RF generator with a system for direct control of the the susceptor temperature.

In order to better evaluate the effect of growth parameter changes on our LEC crystals, several additional characterization techniques will be employed. An x-ray topography system that was recently put into operation has already

allowed the observation of twins, growth striations, and dislocations in transmission experiments on longitudinal sections of several LEC boules. Some of the twins observed by this technique were not visible on etched or lapped surfaces. Transmission topographs will now be used routinely to obtain data for optimizing the LEC growth parameters. A CO_2 laser scanning system has been set up for monitoring the spatial variation in impurity concentration by measuring the free-carrier optical absorption. Finally, transmission electron microscopy will be used to check for micro-precipitates, which have been observed in InP crystals by Cockayne, et al.[10]

REFERENCES

1. H. Gottschalk, G. Patzer, and M. Alexander, Phys. Status Solidi(a) 45, 207 (1978).
2. G. A. Antypas, Inst. Phys. Conf. Ser. No. 33B, Chap. 1, 55 (1977).
3. V. M. Astakhov, L. F. Vasileva, Yu. G. Sidorov, and S. I. Tenin, Fiz. Tverd. Tela 22, 477 (1980).
4. Y. Seki, H. Watanabe, and J. Matsui, J. Appl. Phys. 49, 822 (1978).
5. S. F. Nygren, J. Cryst. Growth 19, 21 (1973).
6. W. A. Bonner, Mater. Res. Bull. 15, 63 (1980).
7. G. K. Ippolitova, E. M. Omelyanovskii, N. M. Pavlov, A. Y. Nashelskii, and S. U. Yakobsen, Sov. Phys.-Semicond. 11, 773 (1977).
8. G. W. Iseler, Inst. Phys. Conf. Ser. No. 45, Chap. 2, 144 (1979).
9. T. Abe, J. Cryst. Growth 24/25, 463 (1974).
10. B. Cockayne, W. R. MacEwan and G. T. Brown, Proceedings of the 1980 NATO InP Workshop (June, 1980), p. 29, RADC-TM-80-07.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 18 ESD-TR-80-231	2. GOVT ACCESSION NO. AD-A096 006	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* 6 InP Materials•		5. TYPE OF REPORT & PERIOD COVERED 9 Annual Technical Summary Report• 1 October 1979 – 30 September 1980
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) 10 Gerald W. Iseler		8. CONTRACT OR GRANT NUMBER(s) 15 F19628-80-C-0002
9. PERFORMING ORGANIZATION NAME AND ADDRESS Lincoln Laboratory, M.I.T. P.O. Box 73 Lexington, MA 02173		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 16 Program Element No. 61102F Project No. 2306
11. CONTROLLING OFFICE NAME AND ADDRESS Rome Air Development Center Griffiss AFB, NY 13440		12. REPORT DATE 11 30 September 1980 13. NUMBER OF PAGES 12 20
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)* Electronic Systems Division Hanscom AFB Bedford, MA 01731		15. SECURITY CLASS. *(of this report)* Unclassified 15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

None

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

InP crystal growth

InP Synthesis

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report covers the work on InP materials carried out with support of the Department of the Air Force during the period 1 October 1979 through 30 September 1980. A part of this support was provided by the Rome Air Development Center. More than half of the synthesized polycrystalline ingots have exhibited mobilities at 77 K greater than 5×10^4 $cm^2V^{-1}sec^{-1}$. From our study of the LEC growth of over 100 InP boules we have found that a high yield of twin-free crystals can be achieved if the axial temperature gradient at the melt interface exceeds a certain minimum value.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED 207650 x1

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

LMED
8